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Water Vapor Adsorption and Hydrogen Peroxide Decomposition on Date Pit Carbonization Products

A. M. Youssef*, Th. El-Nabarawy♠, S. A. Sayed Ahmed and W. E. Rashwan

National Research Centre, Dokki, Cairo, Egypt
*Faculty of Science, Mansoura University, Mansoura, Egypt
♠e-mail: *thoria_elnabarawy@yahoo.com*
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Abstract

Carbonization products C1, C2, C3, C4 and C5 were prepared by the carbonization of date pit in limited air, at 500, 600, 700, 800 and 1000°C, respectively. C1-V-600, C3-V-600, C1-V-1000 and C3-V-1000 were prepared by thermal treatment of C1 and C3 under vacuum at 600 and 1000°C. The textural properties were determined from nitrogen adsorption at 77 K and from carbon dioxide adsorption at 298 K. The surface pH, the FTIR spectra and the acid and base neutralization capacities of some carbons were investigated. The amounts of surface oxygen were determined by out-gassing the carbon-oxygen groups on the surface as CO_2 and CO. The adsorption of water vapor at 308 K on C1, C2, C3 and C4 was measured and the decomposition of H_2O_2 at 308 K was also investigated on C1, C2, C3, C4 and C5. The surface area and the total pore volume decreased with the rise of the carbonization temperature from 500 to 1000°C. The adsorption of water vapor is independent on the textural properties, while it is related to the amount of acidic carbon-oxygen groups on the surface. The catalytic activity of H_2O_2 decomposition does not depend on the textural properties, but directly related to the amount of basic carbon-oxygen complexes out-gassed as CO, at high temperatures.

Keywords *: Carbonized carbon, Modification, Water vapor adsorption, H_2O_2 decomposition*

1. Introduction

Activated carbons (ACs) are highly porous materials which find many applications in various processes related to the adsorption of both gases and solutes from aqueous solutions [1-3]. Coals of different ranks are the most important precursors for the production of activated carbons and lignocelluloses come next to coals in this concern [4, 5]. Recently, numerous attempts have been made to prepare activated carbons from solid wastes [6, 7]. The activated carbons from agricultural and field wastes are most interesting [8-11]. The agricultural and field wastes may represent a solid pollutant to the environment and therefore their use for the production of useful products is highly appreciated. The advantages of agricultural wastes as a carbon feedstock include availability as renewable resources, low ash content, remarkable hardness, and their ability to produce granular activated carbons of high adsorption capacity [12].

Carbons can be treated to exhibit high adsorption capacity for water vapor to replace alumina gel, silica gel and zeolites particularly in atmosphere, medium or conditions where these materials can not be used such as high pH media. Treatment of activated carbons by oxidizing agents such as concentrated nitric acid, persulphates, permanganate and hydrogen peroxide increased the concentration of carbon-oxygen functionality which enhanced water vapor adsorption [13, 14]. The adsorption of water vapor on carbon material was postulated to be dependent on the chemistry of the carbon surface rather than on the textural properties [15].

Carbon materials have also been used for a long time as either direct catalyst or, more frequently as catalyst support. Charcoals and ACs have been shown to exhibit catalytic activity in the decomposition of hydrogen peroxide. The following different factors have been postulated to be effective in this reaction [16]: H_2O_2 concentration, temperature, nature of the carbon surface, medium pH and surface treatment. More recent studies were directed towards applying this type of reaction for practical purposes, especially in problems related to environmental impacts [17-20].

Although activated carbons are widely used as effective adsorbents and catalysts or catalyst supports, their production in some countries (developed countries) is either limited or unknown. The importation of expensive activated carbons represent an economic crisis to some countries. Some Carbonization products with appreciable sorption and/or catalytic activity stimulated many investigations on these low-cost materials that could be simply produced, in one step and with a simple technology [21, 22].

The present investigation reports the adsorption of water vapor at 308 K on carbonization products prepared by carbonization of date pit, in absence of air, at 500~1000°C. The characterization has been also carried out on a few

carbon samples pre-evacuated under reduced pressure at 600 or 1000°C. The decomposition of H_2O_2, in non-buffered aqueous solutions at 308 K by the carbonization products was also investigated. The objectives were to demonstrate the role of (a) carbonization temperature, (b) surface area, (c) chemistry of the surface and (d) surface pH on the kinetics of H_2O_2 decomposition.

2. Experimental

2.1. Materials

2.1.1. Preparation of a carbon stock

A carbon stock was prepared as follows: the raw material (date pit) was first thoroughly washed with distilled water to remove adhering dirt and then oven-dried at 110°C. The dried pit was crushed and milled before carbonization at 450°C in a limited air. This carbon stock was sieved within the 0.1~0.2 mm size fraction.

2.1.2. Modification of the 450°C- carbonization product

The carbon stock was modified by treatment with 10% hot HCl several times followed by treatment with 5% HF and then washed thoroughly with distilled water. This treatment was carried out to minimize the inorganic content which when exists at appreciable concentration may affect water vapor adsorption or catalytic dissociation of H_2O_2. This treatment reduced the inorganic content as evidenced from the ash content which was determined to be 0.117%. Portions from the demineralized stock were carbonized again, in absence of air, at 500, 600, 700, 800 and 1000°C and named as, C1, C2, C3, C4 and C5, respectively. Portions from C1 and C3 were evacuated to 10^{-4} torr at 600°C with a rate of heating = 10°/min and the samples were soaked at 600°C for 1 h more, this gave C1-V-600 and C3-V-600. Other portions were similarly prepared but by evacuation at 1000°C to give C1-V-1000 and C3-V-1000.

2.2. Techniques

2.2.1. Estimation of the combined oxygen

This was made by an apparatus consisting of 50 dm^3-capacity high purity silica reactor leading into two (8.5 dm^3) reservoirs connected to a calibrated Mcleod gauge to measure the pressure of out-gassed CO and CO_2. CO_2 was first solidified in liquid nitrogen trap and the pressure exerted by the out-gassed CO was followed at different temperatures. At the end of the run, the liquid nitrogen trap was replaced by carbon dioxide-acetone freezing mixture to determine the pressure exerted by out-gassed CO_2. The details of this procedure are given elsewhere [23].

2.2.2. pH measurements

These were carried out using PYE-pH-meter on 1 g carbon suspended in CO_2- free doubly distilled water.

2.2.3. FTIR investigation

The FTIR spectra of the carbon samples were obtained using Mattson 5000-FTIR spectrometer using the KBr disc technique. Discs were prepared by first mixing 1 mg of powdered carbon with 500 mg of KBr (Merck; for spectroscopy) in an agate mortar, then pressing the resulting mixture successively under pressure of 5 tons/cm^2 for 5 min and at 10 tons/cm^2 for 5 min, under vacuum. The spectra of the samples were recorded between 4000 and 400 cm^{-1}.

2.2.4. Textural properties.

The textural properties (surface area and porosity) were obtained by measuring the nitrogen adsorption isotherms of the carbons at 77 K, using a conventional volumetric apparatus. The carbon dioxide adsorption isotherms on C1, C2, C3, C4 and C5 were also determined at 298 K, using the same apparatus. Prior to any adsorption measurement, the carbon sample was degassed for 2 h at 200°C under a reduced pressure of 10^{-5} torr.

2.2.5. Base and acid neutralization capacities

The base neutralization capacities (BNC) were determined according to the Boehm titration method [24]. Neutralization was followed using 1.0 M NaOH, Na_2CO_3 and $NaHCO_3$ for the determination of the acid groups whereas 0.1 M HCl was used to neutralize the total basicity of the carbon surface. 0.25 g of the carbon was mixed with 50 ml of the respective solution in 100 ml Quickfit polyethylene bottle. The suspensions were flushed with nitrogen. Mechanical shaking was continued for 48 h. The residual concentration of each solution was determined. Details of the methods are given elsewhere [21].

2.2.6. Adsorption of water vapor

The adsorption of water vapor at 308 K on C1, C2, C3 and C4 was carried out using silica spring balances. The adsorption of water vapor at 308 K on C1, C2, C3 and C4 was carried out with the aid of quartz spring balances of the McBain-Bakr type [25]. The apparatus is enclosed in an air thermostat at 35°C ± 0.1°C. The pressure measurements were made with the aid of cathetometer graduated to 0.02 mm and the measurements was corrected for mercury depression. The cathetometer was also used for the determination of expansions and contractions in the springs due to adsorption or desorption of water vapor, respectively. Corrections for buoyancy effect was considered for the gravimetric determinations [26, 27]. The carbon sample was evacuated to 10^{-5} torr at 150°C for 6h before carrying out water vapor adsorption.

2.2.7. Decomposition of H_2O_2

The decomposition of H_2O_2 at 308 K was determined in non-buffered aqueous solutions. In each experiment 20 mg of powdered carbon were added to 10 ml of fresh 10% H_2O_2 (complete decomposition evolved 300 cm^3 of O_2). The volume of oxygen evolved was recorded with time. All experiments were repeated twice so that data obtained are the mean of two determinations, the deviation did not exceed 1%. Details of the technique and measurements are reported elsewhere [28].

3. Results and Discussion

3.1. Textural properties

The surface area and porosity of carbons are prominent factors in determining their adsorption capacity [29]. In some reactions, the surface area of the carbons has been postulated to determine its catalytic activity [16]. The textural properties of solids are conventionally determined from the adsorption of nitrogen at 77 K and the adsorption data are usually analyzed by the application of the BET equation [30]. However, for micro-porous carbons and zeolites the adsorption of carbon dioxide at 298 K was recommended to replace nitrogen.

The adsorption of nitrogen at 77 K was found to be relatively rapid with the equilibrium attained within 30 min indicating that the adsorption is not controlled by activated diffusion encountered in ultra-fine pores and meanwhile refers to the accessibility of all pores to nitrogen molecules [31]. The isotherms are type I and are characterized by very steep initial portions, well developed knee bend and extended plateau covering a wide range of relative pressure, Fig. 1. The surface areas S^{BET} were calculated by applying the BET equation. The total pore volumes V_t were calculated from the volume of liquid nitrogen adsorbed at P/P_o = 0.95. The mean pore radius r_m was calculated from the relationship:

$$r_m\ (nm) = 2\ V_t\ (ml/g) \times 10^3/S^{BET}\ (m^2/g).$$

The textural parameters are listed in Table 1. Included also

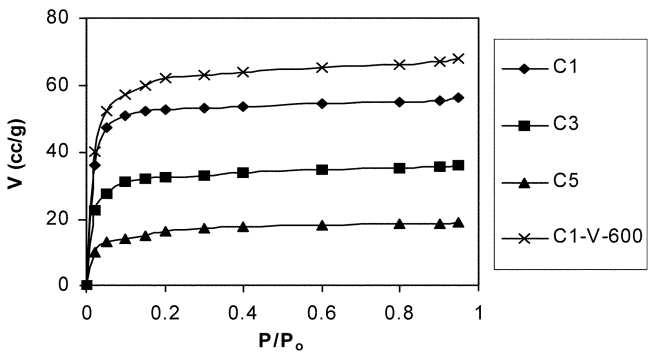

Fig. 1. Representative nitrogen adsorption isotherms at 77 K.

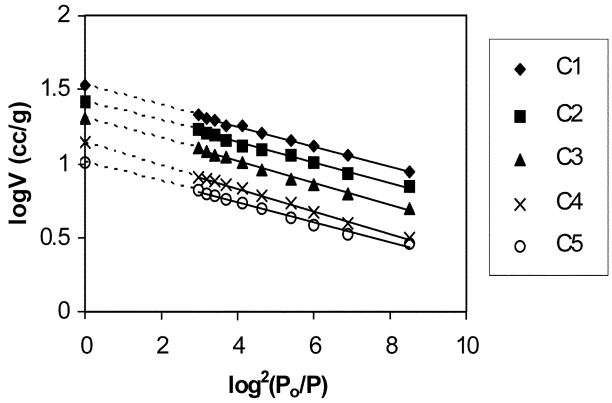

Fig. 2. Representative DR plots for carbon dioxide adsorption at 298 K.

in this table are the micro-pore volumes $V_o^{0.1}$, the volume of nitrogen adsorbed at P/P_o=0.1. Dubinin [32] criticized the application of the BET equation to adsorption in micro-pores and assumed that adsorption in micro-pores proceeds through micro-pore filling rather than surface coverage as assumed by the BET- model. The adsorption of carbon dioxide at 298 K on C1, C2, C3, C4 and C5 was carried out and the data were analyzed by the application of the D-R equation (33). Fig. 2 shows the linear D-R plots which allowed the determination of the micro-pore volume V_o^{DR} and the equivalent

Table 1. Textural properties of the investigated carbons

Sample	S^{BET} m^2/g	V_t ml/g	r_m nm	$V_o^{0.1}$ ml/g	V_o^{DR} ml/g	S^{DR} m^2/g
C1	219	0.088	0.80	0.079	0.080	235
C2	164	0.069	0.84	0.060	0.061	179
C3	131	0.056	0.85	0.048	0.048	141
C4	96	0.043	0.90	0.036	0.033	97
C5	65	0.030	0.95	0.024	0.025	73
C1-V-600	234	0.105	0.91	0.090		
C3-V-600	140	0.067	0.95	0.039		
C1-V-1000	70	0.034	0.96	0.029		
C3-V-1000	61	0.029	0.98	0.024		

surface area S^{DR}, these two parameters are listed in Table 1.

It is evident from Table 1 that: (1) Comparable surface areas are obtained from nitrogen adsorption at 77 K and from carbon dioxiode adsorption at 298 K. The micro-pore volumes of $V_o^{0.1}$ and V_o^{DR} are also comparable. This indicates that nitrogen and carbon dioxide are both physically adsorbed and that most of the surface area measured is located in micro-pores. The agreement between surface areas calculated by the application of the D-R equation and those calculated by the BET equation, may seem astonishing, because these equation are based on two different models .The disagreement between the surface areas calculated by these two methods was ascribed only to the existence of ultra-fine pores [34]. (2) The surface area and the total pore volume decreased while the mean pore radius slightly increased with the rise of the carbonization temperature. (3) Evacuation of C1 and C3 at 600C (C1-V-600 and C3-V-600) was found to result in about 7% increase in S^{BET}, while their evacuation at 1000°C resulted in a drastic decrease in S^{BET}, as a matter of fact the 1000°C-evacuated C1 and C3 should be compared with samples carbonized at 1000°C. Thermal treatment of carbonaceous materials at temperatures ≥ 1000 °C is always accompanied by thermal shrinkage [35].

3.2. Chemistry of the carbon surfaces

The chemistry of the surface of a carbon is equally important to its textural properties in determining its adsorption properties and its catalytic activity, particularly in aqueous solutions. The chemistry of a carbon surface is attributed to the existence of carbon-oxygen functional groups of acidic or basic nature. The pH of the aqueous slurry of the carbon material provides a qualitative indicator of the nature of the surface groups. The FTIR spectra of carbons may give also another qualitative indicator. The quantitative measures of the type and amount of the surface groups, particularly those of carbon-oxygen type could be obtained from the base neutralization capacities adopted by Boehm [24]. It was assumed that $NaHCO_3$ neutralizes carboxylic groups whereas those neutralized by Na_2CO_3 but not by $NaHCO_3$ were believed to be lactones. The weakly acidic groups neutralized by NaOH but not by Na_2CO_3 were postulated as phenols. The total basicity (m equiv./g) was determined from neutralization with 0.1 M HCl. Table 2 give the surface pH and the type and amount of the surface groups. The total amount of the surface carbon-oxygen complexes could be determined by out-gassing the carbon sample at high temperatures (up to 1000°C). The amount of the complexes which is out-gassed as CO could be followed with the rise of the out-gassing temperature from 300 to 1000°C, by measuring the pressure exerted by out-gassed CO by means of the McLeod gauge. The amount of CO_2 could be determined at the end of the experiment. The gas produced was converted to equivalent oxygen concentration assuming that the complex consisted of one oxygen atom [36]. The CO and CO_2 evolved are given in Table 2.

Inspection of Table 2 reveals that: (1) carbonization of date pits at 500~700°C gave carbons with mainly acidic surfaces as depicted from the surface pH. Carbonization at higher temperatures (C4 and C5) gave carbons with considerable surface basicity. The acidic groups (carboxylic, lactonic and phenolic), decreased with the rise of the carbonization temperature, the decrease is more pronounced for carboxylic groups. The basic groups predominated on the surface of carbons prepared at 800 and 1000°C. (2) the amount of CO_2 evolved on out-gassing a carbon sample (m equiv./g) was more or less equal to the total amount of the acid groups expressed in the same units. The total amount of CO evolved (mequiv./g) was found to be of the same order of magnitude as the total basicity determined by neutralization with HCl.

The existence of carbon-oxygen functional groups has been demonstrated from the FTIR patterns (not illustrated) of some selected carbons. The bands in the region above 3000 cm^{-1}, appearing as intense and broad peaks, are attributed to the stretching vibration of hydroxyl groups involved in hydrogen bonding, probably with the participation of water adsorbed on carbon [37]. This absorption band is absent in the 1000°C-char probably due to its low surface area as well as to its typically hydrophobic surface. The shoulders observed at 2920 and 2360 cm^{-1} are usually

Table 2. Surface pH and surface chemistry of the carbons investigated

Sample	PH	Carboxylic mequiv/g	Lactonic meuiv/g	phenolic mequiv/g	Basic mequiv/g	CO_2 evol mequiv/g	CO evol. Mequiv/g
C1	5.6	1.20	0.73	0.90	0.075	2.95	0.08
C2	6.4	0.81	0.50	0.70	0.140	2.05	0.14
C3	6.8	0.52	0.26	0.35	0.260	1.16	0.26
C4	7.6	0.13	0.23	0.27	0.480	0.65	0.47
C5	8.5	–	0.09	0.11	0.700	0.20	0.76
C1-V-600	6.8	0.16	0.22	0.26	0.080	0.66	0.08
C3-V-600	7.1	0.10	0.14	0.25	0.140	0.52	0.13
C1-V-1000	7.9	–	–	–	–	–	–
C3-V-1000	8.5	–	–	–	–	–	–

ascribed to aliphatic compounds and appeared for all the carbons investigated. The most pronounced changes were observed within two absorption bands at 1825~1340 and 1300~1000 cm^{-1}. The former is characteristic of C-O- and N-O- combining structures and the latter may be assigned to cyclic ether containing COCOC groups [38]. The band centered at 1720 cm^{-1} is ascribed to the stretching vibration of the carboxylic acid and lactone groups [39]. The intensity of this band was quite high in C1, C2 and considerably decreased in C3 and disappeared in C4. As a matter of fact, in most cases the location of the absorption band was only taken as a qualitative indicator for the existence of a specific group.

3.3. Water vapor adsorption

The isotherms of water vapor adsorption at 308 K on C1, C2 C3 and C4, are shown in Fig. 3. The surface areas were calculated by applying the BET-equation, adopting the value of 0.106 nm^2 for the cross sectional area of water molecule. The BET-equation was applied to adsorption measurements in the relative pressure range 0.05~0.35, i.e, at pressures where no water condensation is expected. The calculated surface areas are listed in column 2 of Table 3. Included also in this table are the BET-C constants (column 3). Because the isotherms are different in shape, the ratio $a_{0.95}/a_{0.10}$ was calculated for each isotherm (column 4 of table 3). $a_{0.95}$ and $a_{0.10}$ are the amount of water vapor adsorbed at p/po=0.95 and 0.10, respectively.

Table 3 depicted that the water vapor surface areas are very low compared with nitrogen or carbon dioxide surface areas. This indicated that water vapor adsorption is not a function of textural properties. It has been previously report-

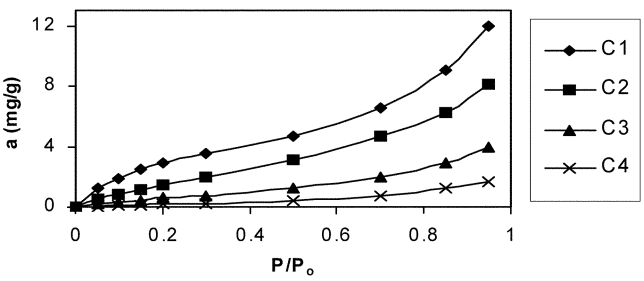

Fig. 3. Water vapor adsorption isotherms at 308K on some selected samples.

Table 3. Adsorption parameters of water vapor on C1-C4

Sample	S^{BET} (m^2/g)	BET-C constant	$a_{0.95}/a_{0.10}$
C1	10.4	13.0	6.3
C2	6.6	7.5	9.5
C3	2.7	5.5	12.0
C4	0.8	5.0	15.0

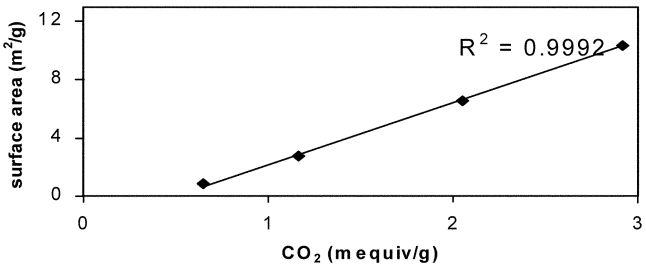

Fig. 4. water vapor surface area Vs out-gassed carbon dioxide.

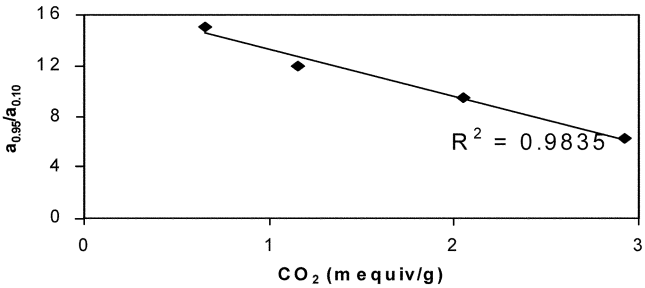

Fig. 5. $a_{0.95}/a_{0.01}$ Vs out-gassed carbon dioxide.

ed that moisture sorption is related to the chemistry of the surface and more specifically to the carbon-oxygen functional groups on the surface [15]. These groups were assumed to be the adsorption sites of water molecules upon which water vapor adsorption is enhanced via hydrogen bonding. This stimulated searching for a relationship between the water sorption capacity of the carbons investigated and any of their surface chemical parameters. The most successful relationship was found between the surface areas determined from water vapor adsorption and the amount of CO_2 out-gassed on evacuation up to 1000°C. Fig. 4, shows that the relationship could be represented by a straight line. The expansion of this straight line to zero water adsorption (complete hydrophobicity) intersected the out-gassed CO_2- axis at 0.5 m equiv./g, which indicated that a critical concentration of acidic carbon-oxygen complexes should be exceeded for the carbon to show hydrophilicity. It is also interesting to report that a linear relation was obtained to indicate a reverse proportionality between the amount of CO_2 out-gassed and the ratio $a_{0.95}/a_{0.10}$ Fig. 5. This relationship indicated that water vapor adsorption on oxygen-poor carbon surface is more enhanced at high relative pressures.

3.4. Decomposition of hydrogen peroxide

It has been assumed that the decomposition of H_2O_2 by carbons involves primary exchange of oxonium hydroxyl group with a hydrogen peroxide anion [16]. This assumption predicted that in an alkaline medium the dissociation of H_2O_2 will be enhanced. The alkalinity is favored either in the solution or on the carbon surface. Based on this, one can

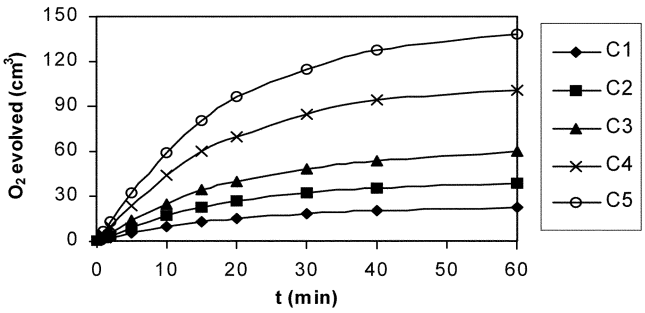

Fig. 6. Kinetic decomposition of H_2O_2 at 308 K on C1-C5.

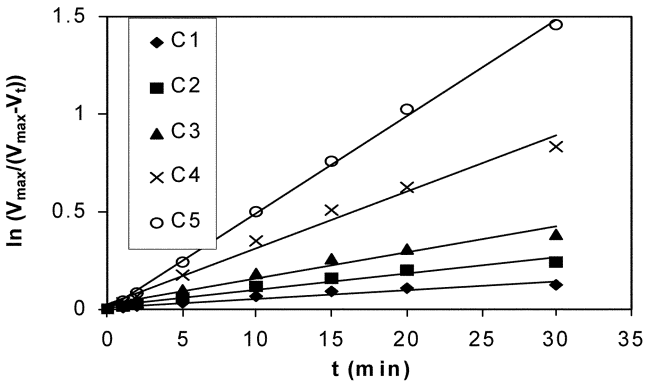

Fig. 7. First order plots for the decomposition of H_2O_2 at 308 K.

predict that the chemistry of the carbon surface is a prominent factor in determining the H_2O_2 decomposition activity of the carbon. Moreover, one could also predict that in the present investigation in which the decomposition is followed in non-buffered solution that the disproportionation of H_2O_2 will be enhanced by the surface basicity and will be suppressed with the surface acidity.

Fig. 6, demonstrates the kinetic oxygen evolution curves at 308 K and shows high slopes of the plots at and beyond 30 min of contact. This might be attributed to the existence of H_2O_2 catalytic sites of different activities. Assuming that the overall heterogeneous decomposition of H_2O_2 is represented by the equation :

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 ,$$

one can calculate the stoichiometric volume of oxygen evolved as V_{max}, the volume of O_2 evolved up to time (t) is considered as V_t, the specific rate constant for each carbon investigated (k, min^{-1}) was determined from the plots of ln $V_{max}/V_{max}–V_t$ vesus t, Fig. 7. Another kinetic parameters were also considered, these are the volume of O_2 evolved at t= 1 h and the % decomposition at t = 1 h. These kinetic parameters are given in columns 3 and 4 of Table 4, respectively. Included also in this Table are the amounts of CO out-gassed up to 1000°C, expressed in mequiv./g.

Evidently, a straight line with a good fitness (R2 = 0.9991) was obtained, Fig. 8, when the values of the specific rate

Table 4. Kinetic parameters of H_2O_2 decomposition at 308 K

Sample	K (min^{-1}) $\times 10^3$	V at 1 h	% decomp. at 1 hr	CO evolved m equiv./g
C1	6.1	22.5	7.5	0.08
C2	10.7	39.0	13.0	0.14
C3	17.1	60.0	20.0	0.26
C4	31.5	101.0	33.7	0.47
C5	51.0	138.0	46.0	0.76

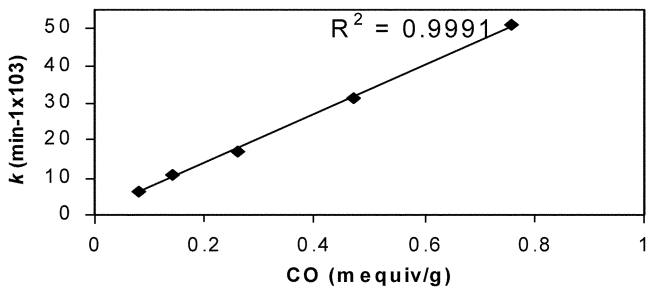

Fig. 8. Rate constant K Vs out-gassed carbon monoxide.

constants (column 2 of Table 4) were plotted versus out-gassed CO (Column 5 of Table 4). Moreover, this straight line passes through the origin indicating a direct relation between the surface basicity and the activity of the carbon towards H_2O_2 decomposition.

4. Conclusions

The textural properties and the chemistry of the surface of the carbonization products depend on the carbonization temperature. The surface area and the total pore volume decreased with the rise of carbonization temperature. The amount of carbon-oxygen groups of acidic nature decreased and those of basic nature increased with the rise of the carbonization temperature. The adsorption of water vapor and the catalytic decomposition of H_2O_2 are independent on the textural properties. The former is related to the amount of carbon-oxygen groups out-gassed as CO_2 while, the latter is directly related to the carbon-oxygen complexes out-gassed as CO.

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